

dilute arsenious acid solution has been determined. With pure materials the blanks, which are purely volume corrections, should be very small, never exceeding a value equivalent to 0.0001 gram As_2O_3 . The author has obtained blanks as low as 0.00004 gram As_2O_3 , which in an analysis requiring 100 cc. of 0.1 N iodine solution amounts to only 0.008 per cent. The blank is always subtracted in calculating an analysis.

15. *Applications of the Method.*—It is evident from the preceding calculations and experiments that under the proper conditions iodine can be quantitatively reduced to iodide by arsenious acid and that a *definite, permanent and exceedingly delicate end-point* is obtained. The accuracy and definiteness of the end-point makes this method a valuable and convenient one for determining the atomic ratio between arsenious acid and iodine since the materials necessary for the determination can be readily purified and the method is free from any sources of error due to side reactions, adsorption, presence of water, etc., which have to be corrected for in many precipitation methods in atomic weight work. The accurate knowledge of this ratio is important to the analytical chemist since arsenious acid is the most convenient and accurate standard for iodimetry.

BOSTON, November 1, 1907.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE SPECIFIC GRAVITIES OF THE IODIDES OF SODIUM, POTASSIUM, RUBIDIUM, CAESIUM, CALCIUM, STRONTIUM AND BARIUM.

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Attention has been recently called by various authors to large discrepancies and inaccuracies in the present tables of specific gravities.¹ If for no other reason, the interest attached to molecular volume² makes the accurate knowledge of specific gravities of considerable importance. Since the specific gravities of the chlorides and bromides of the alkali and alkaline earth metals have already been determined with care,³ the present research is concerned with the iodides of these elements. Lithium iodide was not investigated because its density has recently been found by one of us.⁴

Among the chief sources of error in specific gravity determinations may be mentioned imperfect drying of the substances and inclusion of mother-liquor by crystals. Both these difficulties were avoided in the

¹ Proc. Am. Acad., 31, 163; Am. Chem. J., 31, 220, 229, 538; Trans. Chem. Soc., 91, 56.

² See especially Richards, Proc. Am. Acad., 37, 3, 399; 38, 293; 39, 581.

³ Landolt-Börnstein-Meyerhoffer.

⁴ Baxter, Am. Chem. J., 31, 558.

present research by fusion of the salts, in an atmosphere of nitrogen to prevent decomposition of the iodides.

The purification of the salts from saline impurities and silica is usually of less importance than the elimination of water, since the densities of probable impurities in each case were not far from those of the substances under investigation. Nevertheless, care was taken to remove at least the major part of these impurities.

Of course the usual precautions were taken in setting the pycnometers and in dislodging and boiling out air entangled in the solid material.

The procedure was as follows: The pycnometer employed was devised some years ago for the determination of the specific gravity of very hygroscopic substances,¹ and is a modification of a pycnometer devised by T. W. Richards for the determination of the specific gravity of solids. A weighing bottle was provided with two glass stoppers, one of which was of ordinary shape and was used during the weighing of the substance. Into the other were sealed two capillary tubes which served to fill the bottle with liquid. The weighing bottle and the pycnometer stopper were both made of thick glass in order to avoid distortion when the stopper was inserted. A metallic carriage was used in all the weighings of the bottle.

The salt, contained in a platinum boat, was fused in a current of dry nitrogen in a hard glass tube connected by a ground joint with a bottling apparatus by means of which the boat, after being heated, could be transferred to the weighing bottle without exposure to moist air.² Heat was applied gently at first, till the greater portion of the water had been expelled, then the temperature was increased until fusion had taken place and the fused salt was limpid and free from bubbles of gas. The boat was then allowed to cool in a current of nitrogen and, after the nitrogen had been displaced by dry air, the boat was transferred to the weighing bottle and weighed.

The nitrogen was made by passing air through concentrated ammonia and then over hot copper gauze, and was freed from excess of ammonia, as well as from carbon dioxide and moisture, in the usual way by means of dilute sulphuric acid, potassium hydroxide and concentrated sulphuric acid. In the experiments with barium, strontium and calcium iodides the last traces of moisture were removed from the nitrogen by phosphorus pentoxide. Air was purified and dried with the same reagents as in the case of nitrogen.

After the weighing of the salt, the ordinary stopper was removed, enough toluene to cover the boat and salt was quickly poured into the bottle, and the pycnometer stopper, which had been weighed with a small

¹ Baxter and Hines, *Am. Chem. J.*, **31**, 220 (1904).

² Richards and Parker, *Proc. Am. Acad.*, **32**, 59 (1897)

quantity of sirupy phosphoric acid to make the joint tight, was inserted. The pycnometer was placed in a vacuum desiccator, which was then exhausted, and the toluene was allowed to boil gently for some time with frequent jarring to expel the air contained in the crevices of the salt. By means of the capillary tubes the bottle was completely filled with toluene, and, while the pycnometer was immersed as far as possible in a water thermostat at 25° , the toluene was adjusted to a mark etched upon one of the capillaries. The weight of the system was then determined, after the pycnometer had been wiped with a clean, slightly moist cloth and had been allowed to stand in the balance case for a few moments. Prolonged standing in the balance case produced no difference in weight. After a second adjustment of the toluene the system was again weighed. In every case the two weights agreed within a very few tenths of a milligram. The weight of the pycnometer containing the empty boat and filled with toluene was determined six times. From the average of these six weights,¹ the weight of the salt, and the weight of the system including the salt and filled with toluene, was calculated the specific gravity of the salt.

The toluene was dried over metallic sodium and distilled, the first and last portions being discarded. Its specific gravity was determined by means of an Ostwald pycnometer, the capillaries of which were provided with ground glass caps.

Weight of pycnometer. Grams.	Weight of pycnometer filled with water. Grams.	Weight of water. Grams.	Weight of pycnometer filled with toluene. Grams.	Weight of toluene. Grams.
10.6915	19.4087	8.7172	18.2231	7.5316
....	19.4092	8.7177	18.2237	7.5322
10.5911 (without caps)	19.3091	8.7180	18.1237	7.5326
....	18.1240	7.5329
		Average, 8.7176	Average, 7.5323	
			Volume of water.....	8.7522 cc.
			Weight of toluene in vacuum.....	7.5418 grams
			Density of toluene $25^{\circ}/4^{\circ}$	0.8617

The specific gravity of the toluene was also determined with the pycnometer used in the experiments with the salts.

The close agreement of the results for the density of toluene by the two methods shows that the special pycnometer was yielding satisfactory results.

The weights were carefully standardized to tenths of a milligram, and the corrections of the thermometer at 0° and 32.38° were determined. In the foregoing and in the following tables vacuum corrections were ap-

¹ These weights are given below. Since the platinum boat gradually lost in weight, corrections for this loss and for the toluene displaced by the platinum which disappeared, were applied.

plied as follows: toluene, +0.00126; NaI, +0.00019; KI, +0.00024; RbI, +0.00021; CsI, +0.00012; CaI₂, +0.00016; SrI₂, +0.00012; BaI₂, +0.00009.

Weight of pycnometer and boat. Grams.	Weight of pycnometer and boat, filled with water. Grams.	Weight of pycnometer and boat, filled with toluene. Grams.
22.5227	33.3865	31.9073
....	33.3865	31.9066
....	31.9068
....	31.9066
....	31.9069
....	31.9070
	Average, 33.3865	Average, 31.9069
Weight of water.....		10.8638 grams
Volume of water.....		10.9072 cc.
Weight of toluene in vacuum.....		9.3960 grams
Density of toluene 25°/4°.....		0.8615
Average density of toluene by the two methods.....		0.8616

By evaporating toluene which had been in contact with the fused salts it was shown that all the salts examined are insoluble in toluene.

All the substances were prepared by acting on the carbonates or hydroxides of the metals with pure hydriodic acid and crystallizing the iodides, in most cases twice. This hydriodic acid was made from iodine which had been once distilled from aqueous potassium iodide and once reduced to hydriodic acid with hydrogen sulphide and set free by distilling the hydriodic acid with pure potassium permanganate, with intermediate boiling of the hydriodic acid for some time to remove cyanogen.¹ The final product was thus twice distilled from an iodide, the iodide in the second case being already of considerable purity. Hence chlorine and bromine must have been eliminated.² The iodine was then once distilled from pure water, and again reduced with hydrogen sulphide. The resulting hydriodic acid was filtered to remove sulphur and finally distilled shortly before use, with a quartz condenser. After distillation the acid was always colored brown with free iodine, and the iodides made from it, even after crystallization, showed traces of free iodine. During the fusion of the salts, however, this iodine must have been expelled and any iodates must have been decomposed. The hydriodic acid was free from sulphate.

The salts were all mixed with pure ammonium iodide before fusion, in order to prevent the production of basicity. In the case of the alkalies a very small quantity of ammonium iodide was sufficient to produce the desired effect, but in the case of the alkaline earths even a considerable amount did not completely prevent basicity.

¹ Richards and Singer, *Am. Chem. J.*, **27**, 205.

² Baxter, *Proc. Am. Acad.*, **40**, 421 (1904).

Sodium Iodide.—Commercial sodium carbonate was three times crystallized from aqueous solution in a platinum dish. The carbonate was next dissolved in a slight excess of hydriodic acid and the solution of sodium iodide was evaporated to crystallization in a glass dish. The crystals were freed from mother-liquor by whirling in a platinum centrifugal machine.¹ In many cases the fused material, when dissolved in water and tested with phenolphthalein, gave a slight alkaline reaction. In no case, however, did this alkalinity, which was determined by titration against hundredth-normal acid, correspond to more than five hundredths of a milligram of sodium oxide, hence no measurable effect could have been exerted upon the result.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Grams.	Density of NaI. 25°/4°.
2.9209	0.6879	3.658
1.4635	0.3436	3.670
3.1410	0.7376	3.669
2.5324	0.5953	3.665
4.8574	1.1425	3.663

Average, 3.665²

Potassium Iodide.—Acid potassium carbonate was recrystallized, once in glass and twice in platinum. The final product was then essentially free from sodium. The pure bicarbonate was converted into iodide, as in the case of sodium. The fused material when dissolved in water was neutral to phenolphthalein in every case.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Density of KI. 25°/4°.
3.2078	0.8859	3.120
3.4772	0.9660	3.101
3.2367	0.8948	3.117
2.0803	0.5740	3.123
3.2059	0.8861	3.117
3.1652	0.8759	3.114
3.5595	0.9862	3.110

Average, 3.115³

¹ Richards, *This Journal*, 27, 110 (1905). Baxter and Coffin, *Ibid.*, 28, 1582 (1906).

² Previous determinations of the density of this salt are as follows:

Filhol, *Ann. chim. phys.* [3], 21, 415 (1847) 3.450
Favre and Valson, *Compt. rend.*, 77, 579 (1873) 18°, 3.654

³ Previous determinations of the density of this salt are as follows:

Boullay, *Ann. chim. phys.* [2], 43, 266 (1830) 3.078 and 3.104
Karsten, *Schw. J.*, 65, 394 (1832) 2.908
Playfair and Joule, *Man. Chem. Soc.* 2, 401 (1845) 13°, 3.048 and 3.070
Filhol, *Ann. chim. phys.* [3], 21, 415 (1847) 3.056
Schiff, *Ann.*, 108, 21 (1858) 2.850

Rubidium Iodide.—Rubidium material was purified by five crystallizations as dichloriodide from dilute hydrochloric acid solution. The dichloriodide was dried and converted to chloride by heating to 150°. The chloride was changed to sulphate with sulphuric acid, the sulphate to hydroxide with barium hydroxide, and the excess of barium hydroxide was removed by carbon dioxide. The rubidium hydroxide was neutralized with an excess of hydriodic acid and the iodide crystallized. The fused salt, when dissolved in water, was in every case neutral to phenolphthalein.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Density of Rbi. 25°/4°.
3.0856	0.7741	3.434
3.4762	0.8719	3.435
3.4942	0.8735	3.447
3.2558	0.8156	3.439
3.3482	0.8398	3.435

Average, 3.438¹

Caesium Iodide.—Caesium iodide was made from caesium dichloriodide which had been five times recrystallized.² The dichloriodide was converted to iodide exactly as in the case of rubidium. The fused salt when dissolved in water was in both experiments neutral to phenolphthalein.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Density of Csl. 25°/4°.
4.0805	0.7795	4.510
4.2525	0.8124	4.510

Average, 4.510³

Calcium Iodide.—Marble was dissolved in nitric acid and the solution

Buignet, Jahresb., 14, 15	2.970
Schröder, Ann., 192, 298 (1878)	3.077, 3.081, and 3.083
Spring, Ber., 16, 2724 (1883):	
fused	20°, 3.012
fused, subjected to 20,000 atmospheres pressure	22°, 3.110
fused, twice subjected to pressure	20°, 3.112
Buchanan, Am. J. Sci. [4], 21, 25 (1906), by displacement of mother-liquor	24.3°, 3.043

¹ Previous determinations of the density of this salt are as follows:

Clarke, Am. J. Sci. [3], 13, 293 (1877)	3.023
Setterberg, Oefvers. Stockh. Akad. Förh., 6, 23 (1882)	3.567
Buchanan, Am. J. Sci. [4], 21, 25 (1906), by displacement of mother-liquor	24.3°, 3.428

² Wells, Am. J. Sci. [3], 43, 17 (1892).

³ Previous determinations of the density of this salt are as follows:

Setterberg, Oefvers. Stockh. Akad. Förh., 6, 23 (1882)	4.537
Béketoff, Landolt-Börnstein-Meyerhoffer	4.523
Buchanan, Am. J. Sci. [4], 21, 25 (1906), by displacement of mother-liquor	

was heated with an excess of lime. The filtered solution was acidified and evaporated to crystallization and the product was three times recrystallized.¹ Calcium carbonate was precipitated from the nitrate by means of ammonium carbonate and was thoroughly washed by decantation. The carbonate was then dissolved in hydriodic acid and the iodide crystallized. The salt when fused alone in a current of nitrogen, after solution in water is strongly basic. This basicity was partially remedied by mixing the calcium iodide before fusion with a considerable quantity of ammonium iodide, and keeping the temperature below the sublimation point of ammonium iodide until practically all the water was expelled. The salt was then heated to fusion long enough to eliminate all of the ammonium iodide. The alkalinity of each sample is indicated in terms of calcium oxide in the third column of the table. The density of calcium oxide as given in Landolt-Börnstein-Meyerhoffer is 3.3; hence, the following determinations could not have been appreciably affected by this impurity.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Percent of CaO	Density of CaI ₂ . 25°/4°.
2.1287	0.4636	0.09	3.956
2.1919	0.4777	0.23	3.953
2.5370	0.5523	0.05	3.958

Average, 3.956²

Strontium Iodide.—A solution of strontium chloride was heated first with hydrogen sulphide and then, after filtration, with strontium hydroxide and sulphate.³ From the filtered solution the strontium was precipitated as carbonate with ammonium carbonate, the carbonate was washed and reprecipitated as carbonate. The product, after being washed, was dissolved in hydriodic acid and the iodide was crystallized.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Per cent. of SrO.	Density of SrI ₂ . 25°/4°.
1.9305	0.3657	0.10	4.549
2.2813	0.4323	0.03	4.547
1.8901	0.3573	0.30	4.558
2.2628	0.4284	?	4.551
2.1664	0.4105	0.00	4.547
2.7070	0.5135	0.01	4.542
2.6167	0.4199	0.16	4.549

Average. 4.549⁴

¹ Richards, This Journal, 24, 374 (1902).

² Only one previous determination of the density of this salt exists:

Ruff and Plato, Ber., 35, 3612 (1902)..... 20°, 4.0

³ Richards, Proc. Am. Acad., 30, 375 (1894).

⁴ Bödeker found the value 4.415 at 10°. Die Beziehung zwischen Dichte und

In spite of the addition of ammonium iodide to the salt before fusion, the fused salt was slightly basic in all but one experiment. Since the density of strontium oxide is 4.6,¹ the basicity could not have affected the results.

Barium Iodide.—Barium nitrate was five times crystallized and converted into carbonate by precipitation with ammonium carbonate. From the carbonate the iodide was formed as in the case of calcium and strontium. Here also ammonium iodide failed to prevent basicity completely, but as in the cases of strontium and calcium, the error is too small to consider, since the density of barium oxide is about 5.3.¹

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Percent. of BaO.	Density of BaI ₂ , 25°/4°.
4.8746	0.8110	0.10	5.179
3.9124	0.6551	0.18	5.146
5.0750	0.8525	0.21	5.129
4.3577	0.7292	0.07	5.149
3.9504	0.6615	0.14	5.146
4.3432	0.7270	0.12	5.147
5.0332	0.8414	0.07	5.154

Average, 5.150²

It is to be noted that the values obtained by earlier experimenters are in most cases lower than ours, owing probably to the dangers mentioned at the beginning of this paper.

As a result of this investigation the densities of the following salts at 25° referred to water at 4° were found to be:

Sodium iodide.....	3.665
Potassium iodide.....	3.115
Rubidium iodide.....	3.438
Caesium iodide.....	4.510
Calcium iodide.....	3.956
Strontium iodide.....	4.549
Barium iodide.....	5.150

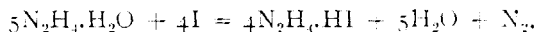
CAMBRIDGE, MASS.,
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ON THE OXIDATION OF HYDRAZINE. II.

BY A. W. BROWNE AND F. F. SHETTERLY.

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Curtius and Schulz³ have shown that alcoholic solutions of hydrazine hydrate and iodine react quantitatively in accordance with the equation



¹ Landolt-Börnstein-Meyerhoffer.

² Filhol obtained the value 4.917. Ann. chim. phys. [3], 21, 415 (1847).

³ J. pr. Chem. [2], 42, 521-49 (1890).